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PATENT SPECIFICATION

Application Date: Oct. 23, 1937. No. 28995/37. 498,256
" " Aug. 16, 1938. No. 24123/38.
One Complete Specification Left: Aug. 18, 1938.
(Under Section 16 of the Patents and Designs Acts, 1907 to 1932.)
Specification Accepted: Jan. 5, 1939.

PROVISIONAL SPECIFICATION
No. 28995 A.D. 1937.

An Improved Process for Bonding Rubber or the like to Metal

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 32, Osnaburgh Street, London, N.W.1, DOUGLAS FRANK TWISS and FREDERICK ARTHUR JONES, both British Subjects and both of the aforesaid Company's Works at Fort Dunlop, Erdington, Birmingham, in the County of Warwick, do hereby declare the nature of this invention to be as follows:—

This invention concerns an improved process for bonding compositions of or containing rubber, gutta-percha, balata to metallic surfaces.

It is known that a film of copper will improve the attachment of rubber to metal such as iron or steel, and it has been proposed to coat iron, steel or tin articles with a thin film of copper, for example by dipping them into a prepared solution of copper sulphate, and then coating them with rubber which is subsequently vulcanised.

In another process rubber is secured to metal by interposing a bonding layer containing organic or inorganic salts of copper or cobalt and subjecting the rubber to heat and pressure.

It has also been proposed to unite vulcanised rubber to metal by interposing a coating of copper, mercury, manganese, or iron salts of organic acids containing one or more reactive groupings in addition to the characteristic acidic grouping and subjecting the rubber applied to the coating to heat and pressure.

It has also been proposed to bond rubber to metal by prior treatment of the former with a halogenated rubber solution. The strength of the rubber-metal bond effected in accordance with the invention about to be described is found to be far greater than can be attained by the use of a metal compound, or of a halogen individually, and is developed immediately thereby permitting the articles to be removed from hot presses without impairment of the bond and without any necessity for preliminary cooling before the press is opened.

[*Price* 1/-]

The improved bond is also capable of withstanding high temperatures, for example temperatures ranging from 100—150° C., without separation and in many cases remains substantially as good at the higher temperatures as at ordinary temperature.

The improved bond is also resistant to vibration, this feature combined with its heat-resistant characteristics rendering such bonds particularly suitable for use in rubber-metal engine mountings for motor vehicles and aircraft in which marked vibration occurs.

According to this invention the method of bonding compositions of or containing vulcanised rubber or the like to metal is characterised by the treatment of the surface or surfaces of the said composition with a solution of a salt containing a heavy metal and one or more free halogens. The halogen or halogens may be applied independently or may be generated in the said solution and more than one halogen may be used concurrently as for example an aqueous solution of a mixture of chlorine and bromine.

The composition of or containing rubber or the like may be suitably compounded and admixed with compounding ingredients including agents of vulcanisation such as sulphur and accelerators prior to effecting the bond by heat and pressure which may incidently assist or complete the vulcanisation of the composition.

The surface of the composition may be treated with the said solution and with the halogen or halogens concurrently or in successive steps, after which the treated surface of the composition is contacted with the metal surface preferably after the latter has been cleaned.

The halogens may be applied as solutions for example, of chlorine or bromine in water. Iodine may also be applied in solution for example in aqueous potassium iodide and mixtures of such solutions may be used.

Examples of suitable salts of heavy metals include:—copper sulphate, cobalt

nitrate, vanadium chloride, chromium chloride, potassium chromate or dichromate, ferric chloride, manganese chloride, gold chloride, mercuric chloride, molybdenum chloride, stannic chloride, antimony chloride, copper acetate, potassium permanganate, ammonium molybdate.

After treating the surface of the composition or the desired portion of the article formed from the said composition with said solution and halogen or halogens, the treated surface or article may be washed in water, and dried, bonding of the treated composition or article to metal being effected when convenient.

The invention may be conveniently carried into effect as follows:

A solution of one or more of the described salts in water is made (for example, 2% concentration) and the halogen added to form an approximately half saturated solution in water. The rubber is immersed in or wetted with this solution for two minutes, washed and dried. Drying can be effected in any convenient manner, for example by mechanical or evaporative methods. The dried rubber is contacted with a steel plate which has been cleaned by convenient means such as " pickling ", sandblasting or rubbing with emery paper or with pumice stone and water, and is then heated in steam or in a press.

In a number of experiments the adhesion was examined at the ordinary temperature and the plate was then heated in an oven at 120° C. for about thirty minutes and the adhesion again examined while hot.

Metal Salt Used.	Halogen.	Adhesion at 20° C.	Adhesion at 120° C.
Cobalt nitrate	None	Very poor	—
None	Chlorine	Very poor	—
Cobalt nitrate	Sodium hypochlorite	Fairly good	Fairly good
Cobalt nitrate	Chlorine	Good	Good
Copper sulphate	Chlorine	Good	Good
Copper sulphate	Bromine	Good	Good
Cobalt nitrate	Bromine	Good	Good
Cobalt nitrate	Iodine in potassium iodide solution	Good	Good
Vanadium chloride	Chlorine	Very good	Very good
Ferric chloride	Chlorine	Good	Good
Nickel sulphate	Chlorine	Slight	Poor
Nickel ethyl sulphate	Chlorine	Slight	Poor
Potassium chromate	Chlorine	Good	Good
Chromium chloride	Chlorine	Fairly good	Fairly good
Manganese chloride	Chlorine	Very good	Very good
Molybdenum chloride	Chlorine	Very good	Very good
Gold chloride	Chlorine	Very good	Very good
Stannic chloride	Chlorine	Good	Good
Mercuric chloride	Chlorine	Good	Good
Antimony chloride	Chlorine	Good	Good

For purposes of comparison similar experiments were made with rubber attached to metal with the aid of chlorides of sulphur:—

Sulphur chloride S_2Cl_2	—	Very poor	—
Sulphur tetrachloride SCl_4	Chlorine	Poor	—

From the above results it will be seen that the adhesion obtained by the use of nickel sulphate or nickel ethyl-sulphate and halogen was very small. Sulphur chloride also either with or without additional halogen gave a very poor adhesion.

Further tests were made and the load necessary for the separation of the metal and rubber both hot and cold was determined the recorded reading being that of the load required to cause slow steady separation of the rubber and metal.

The results obtained are as follows:—

Metal Salt plus chlorine.	Adhesion at 20° C. lbs./linear inch.	Adhesion Hot; Temperature of test	lbs./linear inch.
Stannic chloride	18	115° C.	18
Antimony chloride	20	115° C.	20
Mercury chloride	16	115° C.	12
Molybdenum chloride	40	115° C.	31
Ferric chloride	22	110° C.	22
Vanadium chloride	20	110° C.	18
Copper sulphate	20	120° C.	10
Cobalt nitrate	32	120° C.	16

For the purposes of comparison similar measurements were made with the rubber attached to metal with the aid of bromine water. A similar test was also carried out according to the invention using bromine water and copper acetate solution.

Metal salt plus bromine.	Adhesion at 20° C. lbs./linear inch.	Adhesion Hot; Temperature of test.	lbs./linear inch
Bromine water	14	120° C.	4
Bromine water & copper sulphate	28	120° C.	24

Dated the 22nd day of October, 1937.

W. BOND,
Acting for the Applicants.

PROVISIONAL SPECIFICATION
No. 24123 A.D. 1938.

An Improved Process for Bonding Rubber or the like to Metal

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 32, Osnaburgh Street, London, N.W.1, DOUGLAS FRANK TWISS and FREDERICK ARTHUR JONES, both British Subjects and both of the aforesaid Company's Works at Fort Dunlop, Erdington, Birmingham, in the County of Warwick, do hereby declare the nature of this invention to be as follows:—

This invention concerns an improved process for bonding compositions, of or containing rubber or the like by which is intended natural or synthetic rubber, gutta-percha balata, to metallic surfaces.

It is known that a film of copper or brass will improve the attachment of rubber to metal such as iron or steel, and it has been proposed to coat iron, steel or tin articles with a thin film of copper, for example by dipping them into a prepared solution of copper sulphate, and then coating them with rubber which is subsequently vulcanised.

In another process rubber is secured to metal by interposing a bonding layer containing organic or inorganic salts of copper or cobalt and subjecting the rubber to heat and pressure.

It has also been proposed to unite vulcanised rubber to metal by interposing a coating of copper, mercury, manganese, or iron salts of organic acids containing one or more reactive groupings in addition to the characteristic acidic grouping and subjecting the rubber applied to the coating to heat and pressure.

It has also been proposed to bond rubber to metal by prior treatment of the former with a halogenated rubber solution.

The strength of the rubber-metal bond effected in accordance with the invention about to be described is found to be far greater than can be attained by the use of a metal compound, or of a halogen individually, and is developed immediately, thereby permitting the articles to be removed from hot presses without impairment of the bond and without any necessity for preliminary cooling before the press is opened.

The improved bond is also capable of withstanding high temperatures, for example temperatures ranging from 100—150° C., without separation and in many cases remains substantially as good at the higher temperatures as at ordinary temperature.

The improved bond is also resistant to vibration, this feature combined with its

heat-resistant characteristics rendering such bonds particularly suitable for use in rubber-metal engine mountings for motor vehicles and aircraft in which marked vibration occurs.

According to the invention described in our co-pending application numbered 28995/37 the method of bonding compositions of or containing rubber or the like to metal is characterised by treatment of the surface or surfaces of the composition with a solution of a salt containing a heavy metal and one or more free halogens.

According to the modification introduced by the present invention the method of bonding compositions of or containing rubber or the like to metal comprises treating a surface of said compositions and/or of said metal with a fluid medium containing a compound of a heavy metal and one or more dissolved halogens, bringing the treated surface or surfaces of said compositions and said metal into contact and completing the bond by the application of heat.

The dissolved halogen element or elements may be applied to the surface or surfaces independently of, and before or after the application thereto of the solution or suspension of the compound of the heavy metal, or in admixture therewith. The halogen element or elements may be generated in the said solution and more than one halogen may be used concurrently as for example chlorine and bromine.

The composition of or containing rubber or the like may be suitably compounded and admixed with compounding ingredients including agents of vulcanisation such as sulphur and accelerators prior to effecting the bond by heat and pressure which may incidentally assist or complete the vulcanisation of the composition.

The said medium for preparation of the solution or suspension for the said treatment of the surface or surfaces may be aqueous or otherwise. If the medium used permits it, the solution or suspension for treatment of the surface or surfaces may include additionally a quantity of rubber or a rubber composition which may be a composition similar to that of the rubber surface to be treated.

One or more of the surfaces to be bonded together may be treated with the said solution or suspension and with the halogen element or elements concurrently or in successive steps after which the surfaces are brought together preferably with the aid of pressure and rise of temperature; with either form of procedure the halogen eventually passes into chemical combination in which form it is retained together with the heavy metal between the metal surface and the rubber surface superposed thereon.

The halogens are applied as solutions for example, of chlorine or bromine in water or in an organic solvent such as carbon tetrachloride. Iodine may also be applied in solution for example in aqueous potassium iodide or in an organic solvent such as carbon tetrachloride. Mixtures of such solutions of halogens may be used. The chlorine or other halogen may also, as already described, be introduced into the solutions or suspensions containing already the compound of the heavy metal possibly also together with rubber or rubber composition.

Examples of suitable compounds of heavy metals include:—copper sulphate, cobalt nitrate, vanadium chloride, chromium chloride, potassium chromate or dichromate, ferric chloride, manganese chloride, gold chloride, mercuric chloride, molybdenum chloride, stannic chloride, antimony chloride, copper acetate, potassium permanganate, ammonium molybdate, copper thiosalicylate, cobalt thioglycollate, copper benzoate, cobalt salicylate, cobalt naphthenate, copper pentamethylene-dithiocarbamate, cobalt diethyldithiocarbamate, mercury benzyl-mercaptide, mercury ethylmercaptide, cobalt isopropyl-xanthate.

After treating the surface or surfaces to be bonded with said medium and dissolved halogen or halogens, the treated surface or surfaces may be washed and/or dried, bonding of the surfaces being effected when convenient.

The invention may be conveniently carried into effect as described in the following groups of examples:—

Examples.

Group 1.

A solution or suspension of one or more of the described compounds is made (for example, 2% concentration) and the halogen added to form an approximately one-half per cent. solution. The rubber is immersed in or wetted with this solution for two minutes, washed and dried. Drying can be effected in any convenient manner, for example by mechanical or evaporative methods. The dried rubber is contacted with a steel plate which has been cleaned by convenient means such as "pickling", sandblasting or rubbing with emery paper or with pumice stone and water, and is then heated in steam or in a press.

In a number of experiments using aqueous solutions of the various compounds containing also approximately 0.5% halogen the adhesion was examined

at the ordinary temperature and the plate was then heated in an oven at 120° C. for about thirty minutes and the adhesion again examined while hot.

Metal Compound Used	Halogen.	Adhesion at 20° C.	Adhesion at 120° C.
Cobalt nitrate	None	Very poor	—
None	Chlorine	Very poor	—
Cobalt nitrate	Sodium hypochlorite	Fairly good	Fairly good
Cobalt nitrate	Chlorine	Good	Good
Copper sulphate	Chlorine	Good	Good
Copper sulphate	Bromine	Good	Good
Cobalt nitrate	Bromine	Good	Good
Cobalt nitrate	Iodine in potassium iodide solution	Good	Good
Vanadium chloride	Chlorine	Very good	Very good
Ferric chloride	Chlorine	Good	Good
Nickel sulphate	Chlorine	Slight	Poor
Nickel ethyl sulphate	Chlorine	Slight	Poor
Potassium chromate	Chlorine	Good	Good
Chromium chloride	Chlorine	Fairly good	Fairly good
Manganese chloride	Chlorine	Very good	Very good
Molybdenum chloride	Chlorine	Very good	Very good
Gold chloride	Chlorine	Very good	Very good
Stannic chloride	Chlorine	Good	Good
Mercuric chloride	Chlorine	Good	Good
Antimony chloride	Chlorine	Good	Good

For purposes of comparison similar experiments were made with rubber attached to metal with the aid of chlorides of sulphur:—

Sulphur chloride S_2Cl_2	—	Very poor	—
Sulphur tetrachloride SCl_4	Chlorine	Poor	—

From the above results it will be seen that the adhesion obtained by the use of nickel sulphate or nickel ethyl-sulphate and halogen was very small. Sulphur chloride also either with or without additional halogen gave a very poor adhesion.

Examples.
Group 2.

Further tests were made and the load necessary for the separation of the metal and rubber both hot and cold was determined the recorded reading being that of the load required to cause slow steady separation of the rubber and metal.

The results are obtained as follows:—

Metal Compound plus chlorine	Adhesion at 20° C. lbs./linear inch.	Adhesion Hot; Temperature of test	lbs./linear inch.
Stannic chloride	18	115° C.	18
Antimony chloride	20	115° C.	20
Mercury chloride	16	115° C.	12
Molybdenum chloride	40	115° C.	31
Ferric chloride	22	110° C.	22
Vanadium chloride	20	110° C.	18
Copper sulphate	20	120° C.	10
Cobalt nitrate	32	120° C.	16

Examples.
Group 3

For the purposes of comparison similar measurements were made with the rubber attached to metal with the aid of bromine water. A similar test was also carried out according to the invention using bromine water and copper acetate solution.

Metal Compound plus bromine.	Adhesion at 20° C. lbs./linear inch.	Adhesion Hot; Temperature of test.	lbs./linear inch
Bromine water	14	120° C.	4
Bromine water and copper acetate	28	120° C.	24

EXAMPLES.

GROUP 4.

Adhesion tests were also made on the bonds obtained between rubber and steel and were supplemented by ageing tests both after the treated rubber had been contacted with the metal and vulcanised and by storing the treated unvulcanised rubber for a period of time before the bond was made. The bonds maintain their satisfactory character as is shown by the following observations.

	Adhesion at 70° C.		
Newly bonded specimen		Very good	
After 7 days ageing	do.	do.	Rubber in good condition
After 14 days ageing	do.	do.	do.
After 20 days ageing	do.	do.	do.
After 25 days ageing	do.	do.	Rubber becoming harder and less elastic
After 30 days ageing	do.	do.	Rubber becoming stiff
After 36 days ageing	do.	do.	Rubber stiff and cracked on flexing
After 39 days ageing	do.	do.	Rubber showed marked signs of deterioration

Samples of the treated, but unvulcanised, rubber as above were aged at 70° C. in the Geer oven for a similar period of time; after 30 days ageing the rubber was substantially unchanged, the chemically treated side having aged only to the same extent as the untreated side.

Samples of the unvulcanised rubber were treated (a) with a solution of 10 parts crystallised copper sulphate in 500 parts water to which 100 parts of a saturated solution of bromine in water had been added and (b) with a simlar solution of copper sulphate through which chlorine gas had been passed for 5 minutes. In each case the rubber sheet was immersed in the solutions for 3 minutes. The treated rubbers were stored at 20° C. for 10 months and then were applied to steel plates by vulcanisation of the rubber in contact with the clean plate as previously described.

After vulcanisation the adhesion was determined both at room temperature and at high temperature by the method already described.

The following results were obtained:—

	Adhesion at 20° C.	Adhesion at 112° C.
Copper sulphate and chlorine treatment.	24—28 lbs./inch.	24 lbs./inch.
Copper sulphate and bromine treatment.	40 lbs./inch.	40 lbs./inch.

Steel plates were covered with cobalt nitrate-chlorine treated rubber, copper sulphate-chlorine treated rubber and manganese chloride-chlorine treated rubber. These were subsequently heated in a Geer type ageing oven, maintained at 70° C., for 40 days; at the end of this period the adhesion was still very good both at room temperature and at 110° C. The samples were examined from time to time during the period of ageing and the following observations recorded:—

In spite of the long period of storage before use, the treated rubber ages well either in the vulcanised or unvulcanised condition and the adhesive strength is unimpaired.

EXAMPLES.

GROUP 5.

To a solution of rubber (7.5 parts by weight) in carbon tetrachloride (380 parts by volume) is cautiously added with rapid stirring, a solution of bromine (3 parts by volume) dissolved in carbon tetrachloride (30 parts by volume). A mobile solution is obtained and no separation of clots occurs.

To separate portions of this solution the following additions are made, 0.8 parts (by weight) being added to 100 parts (by volume) of the solution:—

(a) No addition.
(b) Cobalt carbonate.
(c) Copper thiosalicylate.
(d) Cobalt ,,
(e) Cobalt salicylate.
(f) Copper ,,
(g) Cobalt diethyldithiocarbamate.

To further separate portions of the solution the following additions by weight are made per 100 parts of solution by volume:—

(h) Zinc diethyldithiocarbamate (0.45 parts) sulphur (0.25 parts) zinc oxide (0.25 parts) copper thiosalicylate (1.5 parts).
(j) Zinc diethyldithiocarbamate (0.45 parts) sulphur (0.25 parts) zinc oxide (0.25 parts) cobalt thiosalicylate (1.5 parts).
(k) Zinc diethyldithiocarbamate (0.45 parts) sulphur (0.25 parts) zinc oxide (0.25 parts) cobalt salicylate (1.5 parts).
(l) Cobalt diethyldithiocarbamate (1.5 parts) sulphur (0.25 parts) zinc oxide (0.25 parts)

The above mixtures are brushed on clean steel plates and, when dry, layers of unvulcanised compounded rubber are applied. After vulcanising by means of heat and pressure, good adhesion of the rubber to the steel is obtained except in the case of (a) where only very slight adhesion resulted due to the absence of the heavy metal compound. The rubber-covered plates are heated to 105—115° C. for about 30 minutes in an oven and the adhesion is again examined.

Following this outline procedure it is found that the adhesion of the hot bond is substantially as good as that obtained at room temperature (20° C.).

EXAMPLES.

GROUP 6.

Through a solution of rubber (7.5 parts by weight) in carbon tetrachloride (380 parts by volume) chlorine was passed at a rate of about two bubbles per second for about 20 minutes.

To separate portions of this solution 0.8 parts by weight of the following metal salts were added per 100 parts by volume of the solution.

(1) No addition
(2) Copper carbonate.
(3) Copper thiosalicylate.
(4) Cobalt ,,
(5) Copper salicylate.
(6) Cobalt ,,
(7) Cobalt diethyldithiocarbamate.

To separate parts of the chlorine-rubber solution 0.25 parts of sulphur, 0.25 parts of zinc oxide, and 0.45 parts of zinc diethyldithiocarbamate were added per 100 parts by volume of the solution.

(8) Cobalt thiosalicylate 1.5 parts.
(9) Copper ,, 1.5 parts.
(10) Cobalt salicylate 1.5 parts.
(11) Cobalt diethyldithiocarbamate 1.5 parts.
(omitting the zinc diethyldithiocarbamate).

Adhesion tests between rubber and steel were made as previously described and good adhesion both at room temperature and at 115° C. was obtained in all cases except (1) where the adhesion was poor due to the absence of the heavy metal compound.

Dated the 15th day of August, 1938.

W. BOND,
Acting for the Applicants.

COMPLETE SPECIFICATION

An Improved Process for Bonding Rubber or the like to Metal

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 32, Osnaburgh Street, London, N.W.1, DOUGLAS FRANK TWISS and FREDERICK ARTHUR JONES, both British Subjects and both of the aforesaid Company's Works at Fort Dunlop, Erdington, Birmingham, in the County of Warwick, do hereby declare the nature of this invention and in what manner the same is to be performed, to

be particularly described and ascertained in and by the following statement:—

This invention concerns an improved process for bonding compositions of or containing rubber or the like by which is intended natural or synthetic rubber, gutta-percha or balata, to metallic surfaces.

It is known that a film of copper or brass will improve the attachment of rubber to metal such as iron or steel, and it has been proposed to coat iron, steel or tin articles with a thin film of copper, for example by dipping them into a prepared solution of copper sulphate, and then coating them with rubber which is subsequently vulcanised.

In another process rubber is secured to metal by interposing a bonding layer containing organic or inorganic salts of copper or cobalt and subjecting the rubber to heat and pressure.

It has also been proposed to unite vulcanised rubber to metal by interposing a coating of copper, mercury, manganese, or iron salts of organic acids containing one or more reactive groupings in addition to the characteristic acidic grouping and subjecting the rubber applied to the coating to heat and pressure.

It has also been proposed to bond rubber to metal by prior treatment of the former with a halogenated rubber solution.

The strength of the rubber-metal bond effected in accordance with the invention about to be described is found to be far greater that can be attained by the use of a metal compound, or of a halogen individually, and is developed immediately, thereby permitting the articles to be removed from hot presses without impairment of the bond and without any necessity for preliminary cooling before the press is opened.

The improved bond is also capable of withstanding high temperatures, for example temperatures ranging from 100—150° C., without separation and in many cases remains substantially as good at the higher temperatures as at ordinary temperature.

The improved bond is also resistant to vibration, this feature combined with its heat-resistant characteristics rendering such bonds particularly suitable for use in rubber-metal, engine mountings for motor vehicles and aircraft in which marked vibration occurs.

According to the present invention the method of bonding compositions of or containing rubber or the like to metal comprises treating a surface of said compositions and/or of said metal with a fluid medium containing a compound of a heavy metal and one or more dissolved halogens, bringing the treated surface or surfaces of said compositions and said metal into contact and completing the bond by the application of heat.

The dissolved halogen element or elements may be applied to the surface or surfaces independently of, and before or after the application thereto of the solution or suspension of the compound of the heavy metal, or in admixture therewith. The halogen element or elements may be generated in the said solution and more than one halogen may be used concurrently as for example chlorine and bromine.

The composition of or containing rubber or the like may be suitably compounded and admixed with compounding ingredients including agents of vulcanisation such as sulphur and accelerators prior to effecting the bond by heat and pressure which may incidentally assist or complete the vulcanisation of the composition.

The said medium for preparation of the solution or suspension for the said treatment of the surface or surfaces may be aqueous or otherwise. If the medium used permits it, the solution or suspension for treatment of the surface or surfaces may include additionally a quantity of rubber or a rubber composition which may be a composition similar to that of the rubber surface to be treated.

One or more of the surfaces to be bonded together may be treated with the said solution or suspension and with the halogen element or elements concurrently or in successive steps after which the surfaces are brought together preferably with the aid of pressure and rise of temperature; with either form of procedure the halogen eventually passes into chemical combination in which form it is retained together with the heavy metal between the metal surface and the rubber surface superposed thereon.

The halogens are applied as solutions for example, of chlorine or bromine in water or in an organic solvent such as carbon tetrachloride. Iodine may also be applied in solution for example in aqueous potassium iodide or in an organic solvent such as carbon tetrachloride. Mixtures of such solutions of halogens may be used. The chlorine or other halogen may also, as already described, be introduced into the solutions or suspensions containing already the compound of the heavy metal possibly also together with rubber or rubber composition.

Examples of suitable compounds of heavy metals include:—copper sulphate, cobalt nitrate, vanadium chloride, chromium chloride, potassium chromate or dichromate, ferric chloride, manganese chloride, gold chloride, mercuric chloride,

molybdenum chloride, stannic chloride, antimony chloride, copper acetate, potassium permanganate, ammonium molybdate, copper thiosalicylate, cobalt thioglycoliate, copper benzoate, cobalt salicylate, cobalt naphthenate, copper pentamethylene-dithiocarbamate, cobalt diethyldithiocarbamate, mercury benzyl-mercaptide, mercury ethylmercaptide, cobalt isopropyl-xanthate.

After treating the surface or surfaces to be bonded with said medium and dissolved halogen or halogens, the treated surface or surfaces may be washed and/or dried, bonding of the surfaces being effected when convenient.

The invention may be conveniently carried into effect as described in the following groups of examples:—

EXAMPLES.

GROUP 1.

A solution or suspension of one or more of the described compounds is made (for example, 2% concentration) and the halogen added to form an approximately one-half per cent. solution. The rubber is immersed in or wetted with this solution for two minutes, washed and dried. Drying can be effected in any convenient manner, for example by mechanical or evaporative methods. The dried rubber is contacted with a steel plate which has been cleaned by convenient means such as "pickling", sandblasting or rubbing with emery paper or with pumice stone and water, and is then heated in steam or in a press.

In a number of experiments using aqueous solutions of the various compounds containing also approximately 0.5% halogen the adhesion was examined at the ordinary temperature and the plate was then heated in an oven at 120° C. for about thirty minutes and the adhesion again examined while hot.

METAL COMPOUND USED.	HALOGEN.	ADHESION AT 20° C.	ADHESION AT 120° C.
Cobalt nitrate	None	Very poor	—
None	Chlorine	Very poor	—
Cobalt nitrate (acidic solution)	Sodium hypochlorite	Fairly good	Fairly good
Cobalt nitrate	Chlorine	Good	Good
Copper sulphate	Chlorine	Good	Good
Copper sulphate	Bromine	Good	Good
Cobalt nitrate	Bromine	Good	Good
Cobalt nitrate	Iodine in potassium iodide solution	Good	Good
Vanadium chloride	Chlorine	Very good	Very good
Ferric chloride	Chlorine	Good	Good
Nickel sulphate	Chlorine	Slight	Poor
Nickel ethyl-sulphate	Chlorine	Slight	Poor
Potassium chromate	Chlorine	Good	Good
Chromium chloride	Chlorine	Fairly good	Fairly good
Manganese chloride	Chlorine	Very good	Very good
Molybdenum chloride	Chlorine	Very good	Very good
Gold chloride	Chlorine	Very good	Very good
Stannic chloride	Chlorine	Good	Good
Mercuric chloride	Chlorine	Good	Good
Antimony chloride	Chlorine	Good	Good

For purposes of comparison similar experiments were made with rubber attached to metal with the aid of chlorides of sulphur:—

Sulphur chloride S_2Cl_2	—	Very poor	—
Sulphur tetrachloride SCl_4	Chlorine	Poor	—

From the above results it will be seen that the adhesion obtained by the use of nickel sulphate or nickel ethyl-sulphate and halogen was very small. Sulphur chloride also either with or without additional halogen gave a very poor adhesion.

EXAMPLES.

GROUP 2.

The following examples illustrate the use of a fluid medium for treating the surfaces to be bonded, in which a halogen is generated *in situ* by the interaction of

free acid and a substance capable of yielding free halogen, or by the interaction of a hydro-halogen acid and an oxidising agent. The halogen is generated *in situ* in said medium before or concurrently with the treatment of said surfaces therewith.

Unvulcanised rubber treated with mixed solution of :—	Time of Treatment (Minutes)	Adhesion @ 20° C. of rubber to steel after vulcanising	Adhesion at 115° C.
20% aqueous dispersion of bleaching powder 1 part, 10% copper sulphate soln. containing 5% of concentrated hydrochloric acid 1 part.	5	24 lbs. per linear inch	22 lbs. per linear inch
Sodium hypochlorite solution (10% available chlorine) 1 part, 10% solution of cobalt chloride containing 5% of concentrated hydrochloric acid 1 part	10	18 lbs. per linear inch	18 lbs. per linear inch
10% aqueous solution sodium chlorate 1 part, 10% aqueous solution copper sulphate containing 5% of concentrated hydrochloric acid 1 part	30	24 lbs. per linear inch	24 lbs. per linear inch
10% aqueous solution potassium permanganate containing 5% of concenreated hydrochloric acid	2	24 lbs. per linear inch	20 lbs. per linear inch

EXAMPLES.

GROUP 3.

Further tests were made and the load necessary for the separation of the metal and rubber both hot and cold was determined and recorded reading being that of the load required to cause slow steady separation of the rubber and metal.

The results obtained are as follows :—

Metal Compound plus chlorine.	Adhesion at 20° C. lbs./linear inch.	Adhesion Hot: Temperature of test	lbs./linear inch.
Stannic chloride	18	115° C.	18
Antimony chloride	20	115° C.	20
Mercury chloride	16	115° C.	12
Molybdenum chloride	40	115° C.	31
Ferric chloride	22	110° C.	22
Vanadium chloride	20	110° C.	18
Copper sulphate	20	120° C.	10
Cobalt nitrate	32	120° C.	16

EXAMPLES.

GROUP 4.

For the purposes of comparison similar measurements were made with the rubber attached to metal with the aid of bromine water. A similar test was also carried out according to the invention using bromine water and copper acetate solution.

Metal Compound plus bromine.	Adhesion at 20° C. lbs./ linear inch.	Adhesion Hot; Temperature of test.	lbs./linear inch
Bromine water	14	120° C.	4
Bromine water and copper acetate	28	120° C.	24

EXAMPLES
GROUP 5.

Adhesion tests were also made on the bonds obtained between rubber and steel and were supplemented by ageing tests both after the treated rubber had been contacted with the metal and vulcanised and by storing the treated unvulcanised rubber for a period of time before the bond was made. The bonds maintain their satisfactory character as is shown by the following observations.

Newly bonded specimen	Adhesion at 70° C.	Very good
After 7 days ageing	do.	do.	Rubber in good condition
After 14 days ageing	do.	do.	do.
After 20 days ageing	do.	do.	do.
After 25 days ageing	do.	do.	Rubber becoming harder and less elastic
After 30 days ageing	do.	do.	Rubber becoming stiff
After 36 days ageing	do.	do.	Rubber stiff and cracked on flexing
After 39 days ageing	do.	do.	Rubber showed marked signs of deterioration

Samples of the treated, but unvulcanised, rubber as above were aged at 70° C. in the Geer oven for a similar period of time; after 30 days ageing the rubber was substantially unchanged, the chemically treated side having aged only to the same extent as the untreated side.

Samples of the unvulcanised rubber were treated (a) with a solution of 10 parts crystallised copper sulphate in 500 parts water to which 100 parts of a saturated solution of bromine in water had been added and (b) with a similar solution of copper sulphate through which chlorine gas had been passed for 5 minutes. In each case the rubber sheet was immersed in the solutions for 3 minutes. The treated rubbers were stored at 20° C. for 10 months and then were applied to steel plates by vulcanisation of the rubber in contact with the clean plate as previously described.

After vulcanisation the adhesion was determined both at room temperature and at high temperature by the method already described.

The following results were obtained:—

	Adhesion at 20° C.	Adhesion at 112° C.
Copper sulphate and chlorine treatment	24—28 lbs./inch.	24 lbs./inch.
Copper sulphate and bromine treatment	40 lbs./inch.	40 lbs./inch.

Steel plates were covered with cobalt nitrate-chlorine treated rubber, copper sulphate-chlorine treated rubber and manganese chloride-chlorine treated rubber. These were subsequently heated in a Geer type ageing oven, maintained at 70° C., for 40 days; at the end of this period the adhesion was still very good both at room temperature and at 110° C. The samples were examined from time to time during the period of ageing and the following observations recorded:—

In spite of the long period of storage before use, the treated rubber ages well either in the vulcanised or unvulcanised condition and the adhesive strength is unimpaired.

EXAMPLES.

GROUP 6.

To a solution of rubber (7.5 parts by weight) in carbon tetrachloride (380 parts by volume) is cautiously added with rapid stirring, a solution of bromine (3 parts by volume) dissolved in carbon tetrachloride (30 parts by volume). A mobile solution is obtained and no separation of clots occurs.

To separate portions of this solution the following additions are made, 0.8 parts (by weight) being added to 100 parts (by volume) of the solution:—

(a) No addition.
(b) Cobalt carbonate.
(c) Copper thiosalicylate
(d) Cobalt ,,
(e) Cobalt salicylate
(f) Copper ,,
(g) Cobalt diethyldithiocarbamate.

To further separate portions of the solution the following additions by weight are made per 100 parts of solution by volume:—

(h) Zinc diethyldithiocarbamate (0.45 parts) sulphur (0.25 parts) zinc oxide (0.25 parts) copper thiosalicylate (1.5 parts).
(j) Zinc diethyldithiocarbamate (0.45 parts) sulphur (0.25 parts) zinc oxide (0.25 parts) cobalt thiosalicylate (1.5 parts).
(k) Zinc diethyldithiocarbamate (0.45 parts) sulphur (0.25 parts) zinc oxide (0.25 parts) cobalt salicylate (1.5 parts).
(l) Cobalt diethyldithiocarbamate (1.5 parts) sulphur (0.25 parts) zinc oxide (0.25 parts).

The above mixtures are brushed on clean steel plates and, when dry, layers of unvulcanised compounded rubber are applied. After vulcanising by means of heat and pressure, good adhesion of the rubber to the steel is obtained except in the case of (a) where only very slight adhesion resulted due to the absence of the heavy metal compound. The rubber-covered plates are heated to 105—115° C. for about 30 minutes in an oven and the adhesion is again examined.

Following this procedure it is found that the adhesion of the hot bond is substantially as good as that obtained at room temperature (20° C.).

EXAMPLES.

GROUP 7.

Through a solution of rubber (7.5 parts by weight) in carbon tetrachloride (380 parts by volume) chlorine was passed at a rate of about two bubbles per second for about 20 minutes.

To separate portions of this solution 0.8 parts by weight of the following metal compounds were added per 100 parts by volume of the solution.

(1) No addition
(2) Cobalt carbonate.
(3) Copper thiosalicylate.
(4) Cobalt ,,
(5) Copper salicylate.
(6) Cobalt ,,
(7) Cobalt diethyldithiocarbamate.

To separate parts of the chlorine-rubber solution 0.25 parts of sulphur, 0.25 parts of zinc oxide, and 0.45 parts of zinc diethyldithiocarbamate were added per 100 parts by volume of the solution.

(8) Cobalt thiosalicylate 1.5 parts.
(9) Copper ,, 1.5 parts.
(10) Cobalt salicylate 1.5 parts.
(11) Cobalt diethyldithiocarbamate 1.5 parts (omitting the zinc diethyldithiocarbamate).

Adhesion tests between rubber and steel were made as previously described and good adhesion both at room temperature and at 115° C. was obtained in all cases except (1) where the adhesion was poor due to the absence of the heavy metal compound.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The method of bonding compositions of or containing rubber or the like to metal comprising treating a surface of said compositions and/or of said metal with a fluid medium containing a compound of a heavy metal and one or more dissolved halogens, bringing the treated surface or surfaces of said compositions and said metal into contact and completing the bond by the application of heat

2. The process as claimed in Claim 1 comprising treating said surface or surfaces with the said medium and with said halogens independently.

3. The process according to either of the preceding claims wherein said halogens are generated in the said medium.

4. The process according to any of the preceding claims wherein compounding ingredients including sulphur and agents

of vulcanisation are admixed with said compositions and vulcanisation of said compositions is effected concurrently with said bonding.

5. The process according to Claim 1 or Claim 2 wherein said medium contains a proportion of rubber or rubber composition.

6. The process of bonding compositions of or containing rubber or the like to metal substantially as described with reference to the accompanying examples.

7. Composite articles of metal and rubber or the like when bonded together by the process claimed in any of the preceding claims.

Dated the 17th day of August, 1938.

W. BOND,
Acting for the Applicants.

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